Chemistry

Janet Raloff and Ivan Amato report from Dallas at the American Chemical Society's spring national meeting

New catalysts scavenge NO_x emissions . . .

Recent data suggest that more aggressive controls on the nitrogen oxides (NO_x) involved in acid rain may also offer a big payoff in smog-ozone prevention (SN: 9/17/88, p.180). By redesigning the catalyst used in one of the most effective commercially available anti-NO_x technologies, chemical engineers at W.R. Grace & Co. in Columbia, Md., have increased its NO_x-breakdown activity by 50 percent, according to L. Louis Hegedus, vice president of research at Grace. Preliminary data suggest this innovation will not only extend the catalyst's life but also broaden the range of industrial conditions under which it can efficiently operate.

While many, though not all, industrial boilers and electric power plants in the United States are subject to federal NO_x limits, none of these limits is so stringent that it requires an add-on pollutant-scavenging device — comparable to a stack-gas scrubber for sulfur dioxide. The same is not true in Japan and West Germany, where selective catalytic reduction (SCR) devices — though fairly expensive — are widely used. The only commercially available exhaust-gas-treatment technology for NO_x, SCR removes about 80 percent of the NO_x emitted by industrial boilers. Because the U.S. government is contemplating more stringent NO_x controls for boilers, Grace — a leading catalyst manufacturer — decided to investigate ways to make SCR technology more economical.

In SCR systems, exhaust gases, together with small quantities of ammonia, pass through a large, porous catalyst. As the gas and ammonia contact vanadium pentoxide on the catalyst's surface, NO_x breaks down to nitrogen gas and water.

Grace computer analyses showed a reengineering of the size of the catalyst pores through which exhaust gases' flow could dramatically increase NO_x breakdown. Though details are proprietary, Hegedus says, catalyst pores had to become more bimodal — meaning a larger proportion of different-sized holes was needed. Though existing SCR catalysts are slightly bimodal, Hegedus says they should be drastically more so, with the trend toward inclusion of more large pores. However, the titanium dioxide, which supports the catalytically active vanadium pentoxide, was too crumbly to be reconfigured with the necessary pore changes, he says. So Grace engineers built new catalyst blocks of silica, then covered them with the titanium and vanadium layers. A pilot plant to test the new catalyst under typical industrial conditions should begin operating within a year.

. . . and toxic chemicals from the blood

Biochemical engineers at the Massachusetts Institute of Technology in Cambridge have covalently bonded microscopic plastic beads to enzymes derived from microbes. In animal tests, blood filters containing the bead-bound enzymes efficiently and selectively broke down the chemicals against which they were targeted, reports Robert Langer, leader of the filtering systems' design team.

In tests with about 50 sheep, external blood filters containing the bacterial enzyme heparinase removed 99 percent of the anticoagulant drug heparin within about 15 minutes. In similar experiments using 20 rats with jaundice — caused by a toxic buildup of bilirubin (a brain-damaging, yellow degradation product of hemoglobin) — a bead-bound fungal enzyme harmlessly broke down all of the bilirubin in filtered blood.

Blood sampled from treated animals showed that 50 percent of the toxic compound — heparin or bilirubin — still circulated in the body, perhaps the result of a replenishing from stored residues in tissues. The enzyme filtering was sufficient, however, to reduce body concentrations to nontoxic levels, Langer notes. He anticipates that heparinase treatment, now under consideration for commercial development, may eventually be used in patients undergoing open-heart surgery. He adds that a similar, quick external filtering of blood from severely jaundiced newborns — perhaps through the umbilicus — may one day eliminate their need for potentially dangerous blood transfusions.

Neural networks predict reactions

When chemists want to synthesize a chemical, they start with commercially available ingredients and then design a sequence of chemical reactions, which they hope will rearrange the starting materials into the desired product. So the more accurately chemists can predict reaction outcomes, the more efficient their syntheses.

A growing branch of artificial intelligence known as neural networks may help chemists make better predictions, according to David W. Elrod, a computational chemist with the Upjohn Co. in Kalamazoo, Mich. He and associates at both Upjohn and Western Michigan University in Kalamazoo report using a neural network, which they simulate and run on a personal computer, to predict outcomes of simple chemical reactions. The network's accuracy matches that of human chemists and surpasses existing computer expert systems, the researchers say.

As a testbed for the neural network approach to predicting reaction products, the scientists chose a well-studied family of reactions known as electrophilic aromatic substitution. These reactions involve chemically displacing one of six hydrogen atoms, each attached to one of the six interbonded carbon atoms forming the hexagonal benzene ring. When a hydrogen atom gives up its spot on the ring, it leaves behind an electron, an attractive target for an electron-seeking, or electrophilic, atom or chemical group.

Often, one of the benzene's six carbons already hosts a "substituent" that governs further substitutions by biasing where on the ring an electron will be available for bonding. One class of substituents — called ortho-para directors — favors further substitutions mostly at the adjacent "ortho" carbon and at the "para" ring-site three carbons away. The other class — called meta directors — favors subsequent substitutions two carbons away at the "meta" ring position.

The best reaction-predicting neural network the researchers have tried so far consists of three layers of units interconnected somewhat like neurons. The 25 units of the input layer contain chemical information about the first ring-substituent. Through synapse-like connections that can either strengthen or weaken, these units funnel into, and collectively either excite or inhibit, each of the middle layer's five members. In a similar way, these units then turn on or off the two output units, which respectively represent ortho-para-directing or meta-directing first substituents.

The researchers "train" the network by plugging chemical information on 32 first substituents into the input layer. The network "learns" by changing the connection strengths between the units of the three layers until the output predictions coincide closely with experimentally determined results of actual reactions. When tested with 13 ring substituents not included in the training set, the network predicted ortho, meta and para product proportions within 20 percent of actual values in 10 cases. That equals the performance by a small set of human chemists and beats out by three an existing conventional computer expert system for predicting reaction outcomes.

Neural networks can help chemists predict reaction outcomes, the researchers conclude. But Elrod says more elaborate networks will have to be developed for use with complicated reactions.